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Photophysical and Redox NIR-Sensitivity Enhancement in Photorefractive Polymer Composites

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Introduction

We discuss in detail the photophysical effect of “gating” for the near infrared (NIR) sensitivity enhancement of photorefractive polymer composites. Gating stands for the preillumination of the recording material at shorter wavelength before writing a hologram. As presented recently it leads to a decrease of the response time by a factor of 40 in a novel photorefractive (PR) composite based on the poly(arylene vinylene) copolymer TPD–PPV yielding a very high NIR sensitivity. The gating effect was found to be reversible and is interpreted by the influence of mobile charge carriers produced by the preillumination. Here we apply different gating schemes and investigate redox-chemical doping of the TPD–PPV polymer to back up the explanation for the gating effect. Furthermore the TPD–PPV material is compared with conventional PR composites based on poly(*N*-vinylcarbazole) (PVK). These materials show a strongly reduced sensitivity compared to the TPD–PPV composite, nevertheless gating effects were also found in the PVK-based materials with charge-generation limited response times.

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Due to its time-integrating character the photorefractive (PR) effect allows holograms with high-index modulation amplitudes to be recorded even at low light levels. Furthermore, the PR effect is reversible, that is, previously recorded holograms can be erased and/or overwritten. These features make PR materials, in particular amorphous organic PR systems, promising for real-time applications such as phase conjugation of object beams^[2] or time-gated holographic imaging (TGHI).^[3]

In organic PR materials—mostly composites^[4]—photoconductivity and electro-optic (EO) response is achieved simply by mixing functional components. Typically, a sensitizer and nonlinear-optical (NLO) chromophores are doped into a hole-conducting polymer host. To record a hologram, the material has to be poled by an external poling field E_{ext} and illuminated with two coherent laser beams, which yield an interference pattern of dark and bright fringes. In the bright regions excitons are formed by absorption processes. The excitons can dissociate under the influence of the poling field E_{ext} , and the mobile charge carriers (mostly holes) are redistributed and become trapped in the dark regions, which leads to an internal space-charge field E_{SC} . The superposition of E_{ext} and E_{SC} acts on the NLO chromophores, modulating the refractive index of the bulk to replicate the interference pattern, as shown in Equation (1).^[5, 6]

$$\Delta n \sim E_{\text{ext}} E_{\text{SC}} r_{\text{EO,eff}} \quad (1)$$

Here, Δn is the index modulation amplitude, $r_{\text{EO,eff}}$ is the effective EO coefficient, which by itself depends on number density of EO chromophores and the photorefractive molecular figure-of-merit of the chromophore.^[6] The external diffraction efficiency η_{ext} in a holographic experiment (see below for details) depends on Δn according to Equations (2a) and (2b).^[7]

$$\eta_{\text{ext}} = R \exp(-\alpha d / \cos \alpha_1) \eta_{\text{int}} \quad (2a)$$

$$\eta_{\text{int}} = \sin^2 \left(\frac{\pi \Delta n d}{\lambda \cos \alpha_1} \right) \quad (2b)$$

Here, η_{int} is the internal diffraction efficiency, α is the absorption coefficient, d is the sample thickness, λ is the laser wavelength, α_1 is the internal angle of the read beam relative to the sample normal, and $R < 1$ is a factor that takes into account reflection losses.

A useful indicator of the performance of a holographic device is the sensitivity. A widely used definition for the sensitivity is Equation (3)

$$S = \frac{\sqrt{\eta_{\text{ext}}(t_{\text{exp}})}}{I_{\text{WB,ext}} t_{\text{exp}}} \quad (3)$$

with $\eta_{\text{ext}}(t_{\text{exp}})$ being the external diffraction efficiency achieved after an exposure time t_{exp} when writing with a total external write-beam intensity $I_{\text{WB,ext}}$.^[8] In organic PR materials, a high sensitivity can be achieved by: i) generating the highest possible PR space-charge field E_{SC} , ii) optimizing the EO chromophores and their orientational mobility in the host matrix, iii) decreasing the absorption losses α , and/or iv) decreasing the exposure time by increasing the recording speed.

We focus on the development of reversible holographic storage devices with high sensitivity in the near infrared (NIR), which are needed for applications such as TGIH on biological samples such as tissue. Also, NIR is an interesting operation wavelength range due to the availability of low-cost high-power laser diodes and sensitive circuit-coupled device (CCD) detectors. Although point (ii), achieving high Δn by optimizing the chromophores and the glass-transition temperature, is well understood,^[6, 9, 10] the sensitivity of organic PR devices in the NIR has been rather low so far due to their long response times. Herein, we discuss in detail a new material in which we recently discovered the photo-physical phenomenon of "gating", which simultaneously tackles problems (i), (iii), and (iv) to yield devices with very high NIR sensitivity.

Experimental Section

The eutectic mixture of two azo dyes [2,5-dimethyl-4-(4'-nitrophenylazo)-anisole and 3-methoxy-4-(4'-nitrophenylazo)-anisole, ratio 1:1; 30% wt.]^[11] was added as the EO component for all composites investigated. Azo dyes were used rather than chromophores with higher PR figures of merit^[6, 9, 12] because they have an (irreversible) oxidation potential that is higher than that of the investigated hole conductors. In this way, the chromophores were excluded from participating directly in the charge generation, redistribution, and trapping processes, which allowed us to compare different sensitizer–hole conductor systems without chromophore interaction.

In addition to the TPD–PPV (inset Figure 3b,^[13]) composites, materials based on the conventional hole–conductor poly(*N*-vinyl-carbazole) (PVK) were investigated. Diphenyl phthalate (DPP) was used as a plasticizer for all materials. Due to the higher glass-transition temperature (T_g) of PVK, more DPP had to be added to the PVK-based composites (23 wt.% compared to 13 wt.% in the TPD–PPV composites) to ensure that the orientational mobility of the chromophores was similar in all materials. The orientational mobility was measured using an ellipsometric technique.^[14] The TPD–PPV (PVK)-based composites had a T_g of 10(8) °C [DSC (=differential scanning calorimetry), heating rate +20 K min^{−1}]. Measurements were performed at 22 °C.

TPD–PPV composites were prepared with 1 wt.% of the highly soluble C₆₀ derivative [6,6]phenyl-C61-butyric acid-methyl ester (PCBM)^[15] (material 1) or, without a sensitizer, (material 2). Material 3 was produced by adding a very small amount of the oxidizing agent tri-(4-bromophenyl)-aminium hexachloroantimonate (TBPAAH; Aldrich) to 1 as a redox dopant, which is commonly used in the area

of organic light-emitting diodes (OLEDs).^[16] The electrochemical oxidation potential of TBPAAH is 1.30 V vs. Ag/AgNO₃,^[17] that is, much higher than that of TPD–PPV (0.60 V^[13]). Thus, TBPAAH cations will oxidize the TPD–PPV and become neutral themselves. About one molecule per 10⁴ repeat units of the TPD–PPV was added, which yielded a density of 4×10^{16} cm^{−3} permanent charges.

The PVK-based composites were prepared with 1 wt.% of (2,4,7-trinitro-9-fluorenylidene) malonitrile (TNFM; material 4), PCBM (material 5), or 2,4,7-trinitro-9-fluorenone (TNF; material 6). The absorption coefficients of all composites are listed in Table 1.

Degenerate four-wave mixing experiments were performed in the typical tilted geometry^[4] with a wavelength of 830 nm (40 mW laser diode). Two s-polarized write beams ("1" and "2") with external angles $\alpha_{1(2),\text{ext}} = 50.8(71.1)^\circ$ relative to the sample normal were overlapped in 105 μm -thick polymer films sandwiched between ITO–glass electrodes. Unless stated otherwise, the external write-beam powers were adjusted so that the internal intensities were equal (write-beam ratio $\beta = I_2/I_1 = 1$). This maximizes the contrast $m = 2(I_1 I_2)^{1/2}/(I_1 + I_2)$ of the interference pattern and thus, according to reference [18], the achievable space–charge field E_{SC} . The FWHM of the plane Gaussian writing beams was 0.47 mm. Due to the tilted geometry, the illuminated area was elliptical with a half-maximum surface of 0.273 mm² (0.535 mm²) for the write beam. Reflection losses in the multilayer device prior to entering the composite were calculated to be 13% (33%) for the write beam. A unit of 1 W cm^{−2} total internal intensity corresponds to a total external intensity of 3.27 W cm^{−2}.

For readout a weak p-polarized probe beam (external intensity $I_{\text{R,ext}}$, transmitted and diffracted components $I_{\text{R,trans}}$ and $I_{\text{R,diffr}}$) counter-propagating to write beam 1 was used. The external diffraction efficiency is defined as $\eta \equiv I_{\text{R,diffr}}/I_{\text{R,ext}}$; the internal diffraction efficiency was calculated according to $\eta \equiv I_{\text{R,diffr}}/(I_{\text{R,diffr}} + I_{\text{R,trans}})$.

For measurements of the recording dynamics without preillumination, both write beams were switched on after a prepolarization period of 300 s in the dark, and $I_{\text{R,diffr}}$ was monitored as a function of time. With preillumination two different types of measurements were performed. In the first case the samples were illuminated with write beam 1 during the whole prepolarization period and the writing was initiated by switching on write beam 2. For the second type of experiment (called "gating" hereafter) a pulse from a 633 nm HeNe-laser with duration t_g and intensity I_g was applied at normal incidence at the end of the prepolarization period, and after an adjustable delay t_d both NIR write beams were switched on. As an intuitive metric of comparison for the response times we use $\tau_{50\%}$, the time necessary to reach 50% of the quasi-steady-state diffraction efficiency. To securely ensure quasiequilibrium recording conditions, the NIR write time was

Table 1. Comparison of the different materials investigated: Absorption coefficients α (base e) at 633 and 830 nm, respectively. Exposure times t_{exp} ($t_{\text{exp,g}}$) necessary to reach $\eta_{\text{ext}} = 1\%$ without (with) gating, sensitivity S (S_g) without (with) gating calculated from t_{exp} ($t_{\text{exp,g}}$) according to Equation (3) and ratio S_g/S . Gating conditions: TPD–PPV materials 1 to 3 and PVK/TNFM material 4: $I_g = 2.3 \text{ W cm}^{-2}$, $t_g = 955 \text{ ms}$, $t_d = 0.5 \text{ ms}$; PVK materials 5 and 6: $I_g = 4 \text{ W cm}^{-2}$, $t_g = 17 \text{ s}$, $t_d = 0.5 \text{ ms}$. Write conditions: $I_{\text{WB,ext}} = 3.27 \text{ W cm}^{-2}$, $E_{\text{ext}} = 60 \text{ V } \mu\text{m}^{-1}$ except for the values marked with * where $E_{\text{ext}} = 50 \text{ V } \mu\text{m}^{-1}$.

	TPD–PPV/PCBM (1)	TPD–PPV (2)	TPD–PPV/PCBM doped (3)	PVK/TNFM (4)	PVK/PCBM (5)	PVK/TNF (6)
$\alpha(633 \text{ nm}) [\text{cm}^{-1}]$	155	120	155	73	33	25
$\alpha(830 \text{ nm}) [\text{cm}^{-1}]$	8	4	8	8	1	1
$t_{\text{exp}} [\text{s}]$	0.025 (0.2*)	0.50	0.1*	0.60	70	1500
$t_{\text{exp,g}} [\text{s}]$	0.005 (0.01*)	0.13	0.005*	0.80	4.5	100
$S [\text{cm}^2 \text{J}^{-1}]$	1.2 (0.15*)	0.06	0.3*	0.05	$4.4 \cdot 10^{-4}$	$2.10 \cdot 10^{-5}$
$S_g [\text{cm}^2 \text{J}^{-1}]$	6.1 (3*)	0.24	6*	0.04	$7.10 \cdot 10^{-3}$	$3.10 \cdot 10^{-4}$
S_g/S	5 (20*)	4	20*	0.8	16	15

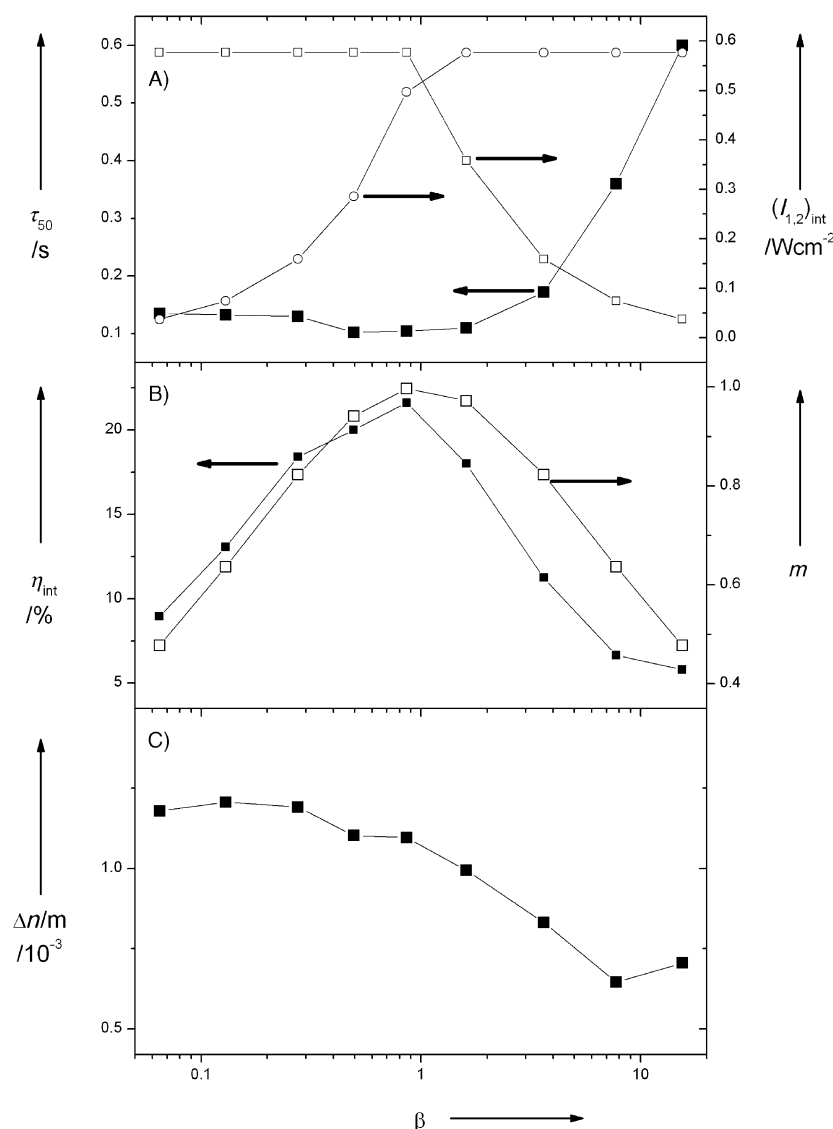


Figure 1. Dependency of the response time τ_{50} (A), of the quasi-steady-state internal diffraction efficiency η_{int} (B) and of $\Delta n/m$, the refractive index modulation amplitude Δn calculated from η_{int} normalized to the grating contrast m , (C) on the ratio β of the internal write beam intensities for the TPD-PPV/PCBM based composite (material 1). Measurements were performed by pre-illumination with beam 1 during a 600 s prepolarizing period ($E_{\text{ext}} = 60 \text{ V}\mu\text{m}^{-1}$) and subsequent opening of beam 2 for a write period of 360 s. Additionally, in part (A) the internal write beam intensities ($I_{1,\text{int}}$ open squares; $I_{2,\text{int}}$ open circles; right hand axis) and in part (B) the contrast factor m of the interference pattern (open squares; right hand axis) are shown. All solid lines are guides to the eye.

60 s except for in the experiments shown in Figure 1. Due to the low intensities used here the write time was increased to 360 s.

The sensitivities were calculated according to Equation (3) for $\eta_{\text{ext}} = 1\%$. This value was chosen to give a three-orders-of-magnitude "buffer" to the minimum required diffraction efficiency for readout with moderate intensities (a few mWcm^{-2}) in a holographic imaging experiment using a standard CCD camera.^[8] This buffer is needed since the experiments presented here are performed under ideal conditions, that is, with plane waves and high contrast of the interference pattern. We use the ratio S_g/S of the sensitivities obtained with and without gating to compare the magnitude of the gating effect.

Results and Discussion

Starting with a pristine sample of the TPD-PPV/PCBM composite 1 we found that after the first experiment performed without any pre-illumination (which yielded $\eta_{\text{int}} \approx 0.19$ and $\tau_{50} \approx 1 \text{ s}$ at $I_{\text{WB,int}} = 1 \text{ Wcm}^{-2}$ and $E_{\text{ext}} = 60 \text{ V}\mu\text{m}^{-1}$), the material experienced a slight but perfectly reproducible performance improvement in consecutive experiments (which yielded $\eta_{\text{int}} \approx 0.22$, $\tau_{50} \approx 0.5 \text{ s}$). Devices could be brought back to the pristine state by melting the composite. The recording dynamics were found to depend sublinearly on the recording intensity. Also, the diffraction efficiency increased with the recording intensity, indicating that E_{SC} is smaller than the limiting value, that is, the projection of the external field onto the grating vector. These findings indicate that the grating build-up is limited by the generation of charge carriers. This is reasonable since the material shows only a small absorption at 830 nm ($\alpha = 8 \text{ cm}^{-1}$, see Table 1), while the redistribution of holes is expected to be fast due to the rather high hole mobility of the TPD-PPV polymer ($\mu_h \approx 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ^[13] compared to $\mu_h \approx 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for the commonly used PVK.^[19]

To accelerate the NIR writing we investigated the influence of preillumination on the material. By using this method, charge carriers are provided before the actual writing process starts, and the charge-generation limit might be overcome.

NIR Preillumination, Dependency on Beam Intensity Ratio

First, experiments were performed in which beam 1 was used for preillumination during the prepolarizing period. Figure 1A shows the dependency of the response time τ_{50} on the write-beam ratio $\beta = I_2/I_1$. Variation of β was achieved by decreasing the intensity of beam 1 for $\beta > 1$ or beam 2 for $\beta < 1$. Under these

conditions τ_{50} showed a strongly asymmetric behavior with respect to β . Keeping beam 1 constant (i.e., constant preillumination intensity, $\beta < 1$) revealed only a small increase in τ_{50} and saturation behavior for small intensities I_2 . We attribute the small increase to the reduction of the total writing intensity (by a factor of two). In contrast, lowering I_1 and keeping I_2 constant ($\beta > 1$) led to a strong increase of the response time (by a factor of six).

The quasi-steady-state diffraction efficiency after 360 s recording was found to decrease for $\beta \neq 1$. This is partly due to the reduced grating contrast m (Figure 1B, open symbols), since it directly influences E_{SC} and thus, Δn as mentioned above.^[18]

However, it is also asymmetrical: for a given contrast a significantly higher Δn was achieved when the preillumination intensity was higher ($\beta < 1$). In order to eliminate the influence of the grating contrast on the performance we calculated the quasi steady-state refractive index modulation amplitude Δn from η_{int} using Equation (2b) and normalized this value using the grating contrast m (Figure 1C). This reveals that the relative grating strength is decreased for $\beta > 1$ as a result of the reduced preillumination intensity. Overall for $\beta = 1$, preillumination by beam 1 yields a fivefold speed enhancement compared to the nonilluminated case.

Preillumination at Shorter Wavelength: "Gating"

We found the preillumination effects to be more pronounced when applying an independent light pulse of shorter wavelength.^[1] We refer to this procedure as "gating" in analogy with the two-color method known from inorganic PR materials^[20] even though the mechanism discussed herein is different.

In Figure 2 the temporal evolution of the diffraction efficiency is shown for the TPD-PPV/PCBM composite **1** for gating with $\lambda = 633$ nm light. Figure 2a shows the results when various

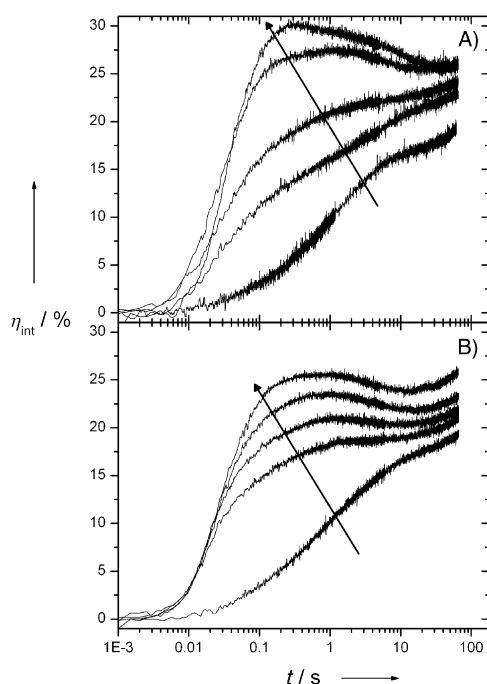


Figure 2. Holographic recording dynamics of **1** for different gate intensities and gate pulse lengths, respectively, with $I_{\text{WB,ext}} = 3.27 \text{ W cm}^{-2}$ and $E_{\text{ext}} = 60 \text{ V } \mu\text{m}^{-1}$. A) Variation of the gate intensity ($I_g = 0, 0.29, 0.58, 2.3$, and 5.2 W cm^{-2}) at a gate pulse length $t_g = 955$ ms. The arrow indicates increasing gate intensity. B) Variation of the gate pulse length ($t_g = 0, 22, 46, 134, 955$ ms) at a gate intensity of $I_g = 4.6 \text{ W cm}^{-2}$. The arrow indicates increasing gate pulse length.

intensities I_g and a constant pulse duration t_g were used, while to generate Figure 2b I_g was kept constant and t_g was varied. A strong increase in the recording speed as well as a slight increase in the quasi-steady-state value of η are observed for both gating methods. For better comparison of the different gating methods,

we plot τ_{50}^{-1} and $\eta_{\text{int}}(t_{\text{exp}} = 60 \text{ s})$ as a function of the illumination dose $I_g \times t_g$ in Figure 3.

The quasi-steady-state value of η_{int} increases by about 40% from the pristine to the strongly preilluminated material (Figure 3B). Most of the performance improvement already occurs for low preillumination doses. Both gating methods yield a similar dependence on the gating fluence. The inverse response times τ_{50}^{-1} (Figure 3A) increase strongly and pass through a maximum corresponding to a response that is 40 times faster than in the nongated material. Surprisingly, about one order of magnitude fewer photons ($0.2 \text{ J cm}^{-2} \approx 6.4 \times 10^{17}$ photons) are necessary to reach this maximum when the devices are illuminated briefly (40 ms) with a high intensity than when they are illuminated for a longer period (≈ 1 s) with lower power ($2.2 \text{ J cm}^{-2} \approx 70.4 \times 10^{17}$ photons). For higher preillumination doses the recording speed decreases slightly and intermediate diffraction maxima are observed in the time traces (e.g. Figure 2A, top curve).

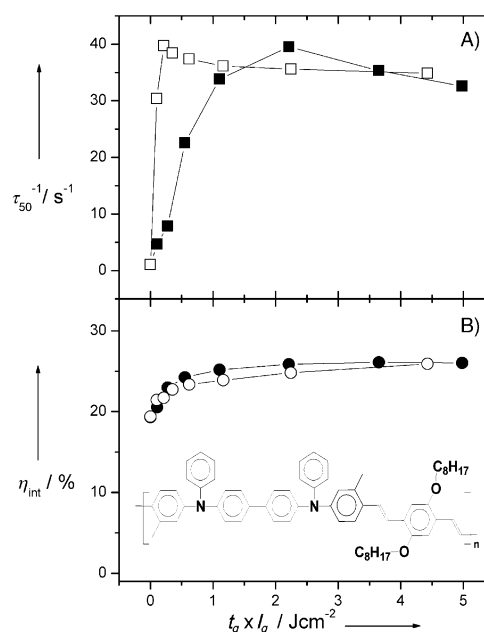


Figure 3. Dependence of the inverse response times τ_{50}^{-1} (A) and of internal diffraction efficiency η_{int} after writing for 60 s (B) to **1** on the gating fluence derived from Figure 2. Solid symbols: constant gating time $t_g = 955$ ms, variation of gate intensity I_g ; open symbols: constant gating intensity $I_g = 4.6 \text{ W cm}^{-2}$, variation of gate pulse length t_g . All solid lines are guides to the eye. Inset (B): chemical structure of TPD-PPV.

The gating effect becomes stronger at lower poling fields (factor ≈ 4 higher S_g/S ratio for $E_{\text{ext}} = 50 \text{ V } \mu\text{m}^{-1}$ compared to $E_{\text{ext}} = 60 \text{ V } \mu\text{m}^{-1}$, see Table 1).

To test the reversibility of the gating procedure, we performed experiments where a temporal delay t_d was introduced between the application of the gate beam and the initiation of the writing process. We found that the recording slows down exponentially, reaching a relaxed state after $t_d \approx 50$ s (Figure 4A) while the quasi-steady-state remains unaffected by the delay time, within experimental error (Figure 4B). However, as mentioned above,

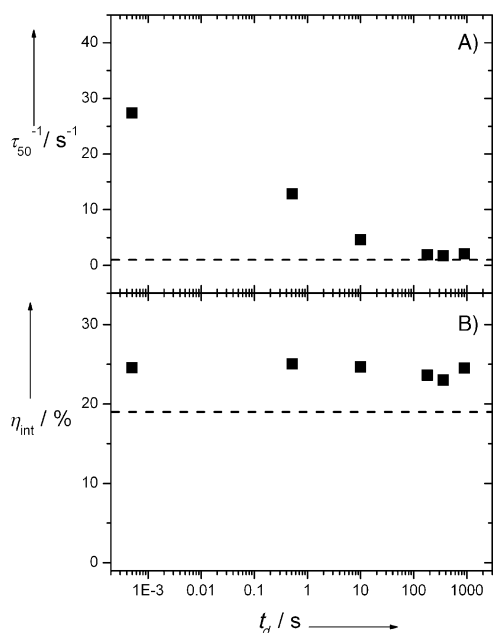


Figure 4. Dependence of the PR performance of 1 on the dark delay (t_d) between gate pulse and writing procedure. Inverse of the response times τ_{50}^{-1} (A) and quasi-steady-state internal diffraction efficiency η_{int} after writing for 60 s (B). Gating conditions: $I_g = 1.2 \text{ W cm}^{-2}$, $t_g = 955 \text{ ms}$, $t_d = 0.5 \text{ ms} - 900 \text{ s}$. $I_{\text{WB,ext}} = 3.27 \text{ W cm}^{-2}$, $E_{\text{ext}} = 60 \text{ V } \mu\text{m}^{-1}$. The dashed horizontal lines mark the τ_{50}^{-1} and η_{int} values for a nongated experiment.

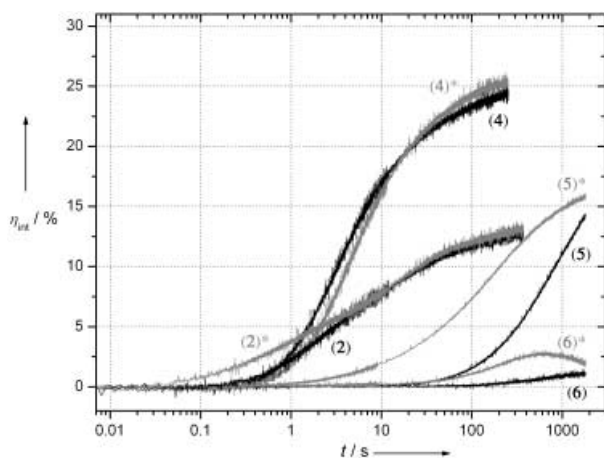


Figure 5. Holographic recording dynamics of the PVK-based composites 4, 5, and 6, sensitized with TNFM, PCBM or TNF, respectively, and of the TPD-PPV material 2 without sensitizer. The curves marked with * were performed with gating, the unmarked curves without gating. Gating conditions: 2 and 4: $I_g = 2.3 \text{ W cm}^{-2}$, $t_g = 955 \text{ ms}$; 5 and 6: $I_g = 4 \text{ W cm}^{-2}$, $t_g = 17 \text{ s}$, $I_{\text{WB,ext}} = 3.27 \text{ W cm}^{-2}$, $E_{\text{ext}} = 60 \text{ V } \mu\text{m}^{-1}$.

even in the relaxed state the recording speed is still a factor of about two faster than in the pristine samples (Figure 4A). These findings indicate a long-term change in the material, which we attribute to the quasi-irreversible filling of the deepest traps in the system. The fact that the response time $1/\tau_{50}$ is affected by the short-term relaxation ($t > 50 \text{ s}$), while the diffraction efficiency η is not, is explained by the fact that the steady state depends on the number density of trapped charges but is independent of

the trap depth the carriers are in, the latter factor being of paramount importance for the dynamics. The time needed for the system to relax to its pristine state is on the scale of months, at least.^[22]

Only a small speed-up effect and no increase in diffraction efficiency upon gating were found for the TPD-PPV material 2 without sensitizer (Figure 5 and Table 1).

Discussion of the Gating Effect

To understand the influence of gating on the response time and the diffraction efficiency, one has to consider the different ways in which the charge-density modulation, or the space-charge field E_{SC} , develops with and without gating. In the ideal case without gating the initial hole density is zero. Mobile holes are generated in the bright regions of the NIR interference pattern and subsequently become redistributed. The charge-density modulation amplitude increases monotonically and relatively slowly until it finally reaches its quasi-steady-state value.

In contrast, using preillumination a uniform space-charge density is formed. These preproduced charges lead to a faster build-up and, at least intermediately, to higher values of the space-charge field E_{SC} during the NIR writing process.

The efficiency of the gating process is higher when short-wavelength light is used, since the carrier generation is much more efficient at shorter than at longer wavelengths. Also, as the generation efficiency ϕ strongly depends on the poling field strength ($\phi \propto E^p$; $p \approx 2.2$ for PVK-based materials^[21]), gating becomes more pronounced for low field strengths. The speed-up effect of the gating is less pronounced for the TPD-PPV material 2 without sensitizer, since here only a few charge carriers are produced by the preillumination.

The preproduced charges increase the number density of PR traps, enabling higher E_{SC} values.^[22, 23] Since the TPD-PPV composite without additional sensitizer (2) shows no change in the quasi-steady-state value of η upon gating (Figure 5), we conclude that, as in reference [23], the traps produced by the preillumination are sensitizer anions recombination centers, that is, PCBM⁻ in the TPD-PPV/PCBM composite.

The fact that gating with high intensity and short pulses is one order of magnitude more efficient than gating with lower intensities and longer pulses clearly indicates some additional dynamic process that the charge carriers undergo during gating and recording. This result is interpreted so that redistribution of the carriers is relatively fast as long as the carriers are mobile (in shallow traps), whereas redistribution becomes increasingly difficult when they are allowed to get trapped in the "deep" tail states of the density of states (DOS) at long time periods.^[24] This relationship is also responsible for the reduction in recording speed at high preexposure doses (Figure 2, 3A), that is, the number density of mobile charge carriers passes through a maximum due to relaxation of the charges in the DOS manifold over time. This speed reduction is also found in the relaxation experiments, where the charges are allowed to recombine and to populate deep traps during the delay time t_d .

Overall, the advancing charge redistribution competes with a decreasing density of charge carriers, and thus, at intermediate

times, the charge density modulation amplitude can assume larger values than in the quasi-steady-state, which is identical to the case without gating.

It follows from the results presented so far that gating is most efficient when: 1) charge generation limits the build-up speed of E_{SC} ; 2) long-lasting charge carriers are generated; and 3) the pre-produced charge-carrier package is not fully relaxed within the DOS, that is, it remains mobile.

We assume that providing a certain amount of charge carriers in a certain time by using a carefully chosen gate pulse changes the trapping landscape by partially filling deep traps while providing sensitizer anions as recombination centers. This way the charge-density modulation can be "carved" into the initial hole density by the NIR pattern, a process which is much faster than starting at zero initial hole density. These assumptions are reinforced by photophysical investigations.^[25]

In all, our findings show that both the build-up speed and quasi-steady-state value of the space-charge field magnitude strongly depend on the preillumination intensity for the TPD–PPV/PCBM composite. However, while η only seems to depend on the number density of preproduced charges, the response time is also sensitive to the energetic state these charges are in. In this context, it is important that the EO chromophores do not constitute hole traps, as is the case here. While an improved Δn upon pre-illumination have been observed before (reference [22]), so far only a deceleration^[22, 26] of the response speed or a modest acceleration accompanied by a high loss in diffraction efficiency^[27] upon preillumination has been reported by other groups.

Comparison with PVK-Based Materials

We also investigated the effect of preillumination on materials based on the commonly used hole-conducting matrix PVK. Three different sensitizers were used: TNFM, TNF, and PCBM. TNFM is the sensitizer usually employed for carbazole-containing hole conductors in the NIR region, while TNF and PCBM are less suited for this region since they do not significantly increase the NIR absorption. A positive gating effect (increased η and reduced response time) was observed only in PVK materials **5** and **6** with the "wrong" NIR sensitizers, PCBM or TNF (Figure 5). These findings prove the above statement that gating enhances the PR performance for charge-generation-limited materials. In contrast, gating leads to a slightly slower E_{SC} build-up in the PVK/TNFM material **6**. We assume that, in this efficiently sensitized material, the response time is not limited by the charge generation but by the charge redistribution (low hole mobility of PVK, see above). In this case, the gating effect discussed here is not revealed. The increase of the response time upon gating could be explained by assuming a reduced hole mobility due to "optical trap activation" (OTA), as reported in reference [22]. OTA also gives rise to a slightly higher quasi-steady-state value of η , as observed here.

The PVK/PCBM material **5** shows a diffraction efficiency 15 times higher than for the PVK/TNF material **6**, despite their similar absorption coefficients. This again shows the important role of the sensitizer on the lifetime of charges. With PCBM the

time-integrating character of the PR effect is more pronounced, allowing a higher space-charge density to be achieved. With TNF fewer long-lasting charge carriers are produced and the lifetime of the carriers is shorter, as can be seen from the rollover of curve **6*** in Figure 5.

Chemical Doping

The beneficial effect on the PR performance of long-lasting charge carriers produced by gating led us to study the redox-chemical doping (oxidation) of material **1** as a way to provide permanent charge carriers. To do so, very small amounts of the oxidizing agent TBPAH were added (see Experimental Section for details). At the low doping levels used here the optical properties of the resulting material **3** were not affected.

Figure 6 compares the nongated and gated performance of the doped material **3** and the nondoped material **1**. Without gating, the doped material has a slightly faster response than the

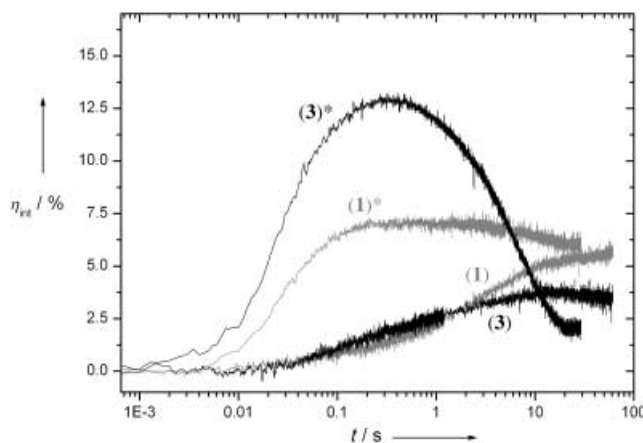


Figure 6. Influence of chemical doping on the holographic performance. Temporal evolution of the internal diffraction efficiency of the undoped (curve **1**) and doped (curve **3**) material. The curves marked with * were performed with gating, the unmarked curves without gating. Gating conditions: $I_g = 2.3 \text{ W cm}^{-2}$, $t_g = 955 \text{ ms}$, $I_{WB,ext} = 3.27 \text{ W cm}^{-2}$, $E_{ext} = 50 \text{ V } \mu\text{m}^{-1}$.

nondoped material as a result of the faster redistribution of pre-existing charges. On the other hand, the doped material has reduced η in the steady state, which we attribute to its increased dark conductivity, as observed experimentally. The most striking result of doping is that, during early stages of the recording ($t < 0.3 \text{ s}$), the gated diffraction efficiency is about two times higher in the doped material, while the quasi-steady-state value is smaller, as discussed above. The intermediate diffraction maximum is much more pronounced than for the nondoped material. This is consistent with our explanation, since, in the doped material, the intermediate carrier density is inherently higher, which allows it to temporarily reach a much higher E_{SC} than in the nondoped material. Unfortunately, the dielectric stability of the composites was reduced by doping.

Magnitude of the Gating Effect

The sensitivities with (S_g) and without (S) gating for all investigated materials are listed in Table 1. Even without gating the TPD-PPV/PCBM material shows a higher sensitivity (by a factor of 24) than the best PVK material, the PVK/TNFM composite. Since the orientational mobility of the chromophores was adjusted to be similar, this is due to a faster E_{SC} build-up in the TPD-PPV matrix. With gating the sensitivity of the TPD-PPV/PCBM material is 120 times higher than for the (nongated) PVK/TNFM composite. The doped TPD-PPV/PCBM composite shows a sensitivity higher by a factor of two compared to the undoped material for both experiments, with and without gating.

In our earlier paper, we had reported $S_g(\eta_{ext} = 1\%) = 19 \text{ cm}^2 \text{ J}^{-1}$ for the TPD-PPV/PCBM composite (material 1) with $I_{WB,ext} = 0.65 \text{ W cm}^{-2}$, $I_g = 2 \text{ W cm}^{-2}$ and $E_{ext} = 60 \text{ V } \mu\text{m}^{-1}$ in a pulsed experiment (90 Hz write rate, during the first quarter of a cycle the gate beam was on while the write beams were on during the remaining time), which is a factor of ≈ 3 higher than for the CW data presented here ($S_g = 6.1 \text{ cm}^2 \text{ J}^{-1}$). There are two reasons for this discrepancy: On the one hand the sensitivity S_g was found to increase when lowering I_{ext} at a constant preillumination intensity (see leveling of τ_{50} in Figure 1a for $\beta < 1$). Thus the higher write intensity $I_{ext} = 3.27 \text{ W cm}^{-2}$ used in the CW experiment yields a smaller S_g . On the other hand, gating is more efficient in the pulsed experiment since the gate pulse is applied here consecutively after a short write phase of a few milliseconds.

Conclusions

While achieving high-refractive-index modulation amplitudes with optimized NLO chromophores and glass-transition temperatures is well understood, this work represents the missing link for achieving high recording speeds in the NIR without loss in transparency. Organic PR materials with charge-generation-limited performance can be "gated" by preillumination, which results in PR devices with unprecedented sensitivity in the NIR. The novel TPD-PPV/PCBM-based composite shows a sensitivity higher by two orders of magnitude in comparison with PVK/TNFM-based materials, the hole-conductor/sensitizer combination commonly used in the NIR. With consecutive gating the TPD-PPV/PCBM devices are about one order of magnitude more sensitive at a given external field than the previously best organic PR devices, a multifunctional glass^[28] and a methine dye.^[29] The latter were about twice as sensitive as the best PVK/TNFM-based systems.^[30, 31] We point out that a true comparison is difficult due to differences in the experimental conditions employed by the different groups, such as device thickness, operating wavelength, and electric field strength.

Gating takes advantage of generating charges at short wavelengths before the actual writing starts, and still recording at a longer wavelength, at which the material is almost transparent. For a given exposure dose, gating was found to be more efficient when using short exposure times and high gate intensities instead of longer exposures at lower intensities.

Redox doping of an organic PR material—presented here for the first time—allowed part of the sensitivity enhancement to be achieved even without preillumination. Additional gating led to further improvement even beyond the best performance of the nondoped material. Future research will aim to optimize the doping level.

The results reported here are very important for applications such as TGH, for example, in biomedical studies such as dermatology. On one hand, a fast recording speed in the NIR is mandatory to avoid motion artifacts. On the other hand, the recording materials need to perform under conditions where the signal is small (weak object beam) and predominantly scattered light is present. Our experiments performed at small contrast of the interference pattern mimic this situation. Thus, the fact that the recording speed is only determined by the preillumination intensity is very important for applications with weak object beams, such as TGH.

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